

Direct Alloying of Steel with Nickel Concentrate

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Abstract. A technology of alloying steel with nickel reduced from nickel concentrate is analysed and developed. Limits of reduction concentration areas are defined. An optimal composition of nickel concentrate pellets and a method of feeding them into the furnace are deduced from experiments. It is proved that when pellets made of nickel concentrate and coke are added into the charge during steel smelting by the technology of alloyed scrap remelting, nickel recovery achieves 92–95%. The technology was tested by smelting DSP-40 steel.

Introduction

Nickel is one of the most important and widely used alloying elements. Alloyed steels and complex iron-nickel alloys production takes from 60 to 65% of the nickel produced per year. The rest 35–40% are used in non-ferrous metallurgy and chemical industry, first of all for making electroplates [1–5]. Steel is usually alloyed with nickel in electric arc furnaces by introducing nickel or ferronickel into the furnace charge. There are no any showings of using nickel oxides or nickel concentrates in domestic metallurgical industry. However, a technology of direct alloying of steel with manganese, chromium and vanadium is successfully used. Advantages of this technology consist in throughout recovery of an alloying element which means eliminating ferroalloy smelting stage and thus leads to cost saving [6, 7]. Nickel production is a resource- and energy-consuming process, which is why application of nickel concentrate for direct alloying of steel can be advantageous. Nickel concentrate consisting of 42–45 % Ni, 2–3 % Mn, 1–1.5 % Fe, 0.3–0.5 % can be produced by complex beneficiation of ferromanganese nodules and polymetallic manganic ferrous materials [5, 8 – 10]. The aim of this work is a scientific justification, research and development of a technology for producing nickel alloy steel using nickel concentrate.

Methods and Materials

When melting steel in arc furnaces, carbon and silicon dissolved in liquid steel can serve as reducing agents at different melting stages.

To determine the conditions under which nickel is reduced from nickel-containing oxide materials we used thermo-dynamic modeling methods based on calculation of equilibrium states in model thermodynamic systems. Calculation of thermodynamic equilibrium reveals a possibility of obtaining



different substances which are important for estimation of the limit state and determines acceptable values. To carry out the thermodynamic modeling we used "Terra" software complex.

Nickel reduction was studied in a three-component system Ni–O–C represented by a set of substances $l\text{NiO} - n\text{C}$, where l – a number of NiO moles, n – a number of carbon moles. Values of l and n were set as a reference composition of the system.

The research procedure involved the following stages: calculating possible compositions and determining thermodynamic conditions required for nickel reduction; determining limits of reduction concentration areas; finding input flow parameters which provide the best composition of the system under equilibrium conditions.

Possible compositions which could result from nickel reduction in thermodynamic system consisting of Ni–O–C and Ni–O–C–Fe were determined by varying the number of carbon moles in the system. It helped us to find the limits of reduction concentration areas. The reference composition of the model system Ni–O–C was the following: 1mole of NiO and n moles of carbon. The calculations were made in the temperature interval from 573 to 1873 K which corresponds to melting temperature.

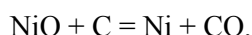
Kinetic laboratory tests of nickel reduction from oxide at the temperature range 973–1473 K were carried out by the method of continuous weighing by a common technique [7].

For treating steel in a ladle, briquettes were composed. They consisted of the nickel concentrate obtained by beneficiation of polymetallic manganiferous materials (% mass. Ni – 45.0, Mn – 2.3, Fe – 1.4, Co – 0.5, Cu – 0.1, P – < 0.015, SiO₂ – other impurities – 2.82) and coke produced by "EVRAZ-ZSMK" Ltd with chemical composition shown in Table 1.

Table 1. Chemical composition of coke by "EVRAZ-ZSMK" Ltd

	A^d	V^{daf}	W^p	Ash composition, % mass									
				SiO ₂	Al ₂ O ₃	MnO ₂	MgO	CaO	Fe ₂ O ₃	P ₂ O ₅	K ₂ O	Na ₂ O	CO ₂
Coke	13.6	2	2	51.1	23.3	0.16	1.58	1.2	17.46	0.5	1.2	0.2	74.4

Proportion of the nickel monoxide and the coke was calculated by the reaction:



The coke and the nickel concentrate were mixed thoroughly. Liquid glass having a density of 1.4 g/cm³ and amounting 5 % of the mass was used as a bonding agent. Briquettes were pressed by a hydraulic press having a tonnage of 10 tons. The briquettes produced were of cylinder shape, 40 cm high and 25 mm in diameter. The briquettes were place in an alundum pot which in its turn was installed into a graphite pot and suspended on a special device in a preheated resistance furnace.

Isometric soaking was carried out at the temperatures of 1073, 1173, 1273 and 1473 K. The thermocouple BP 5.20 was used for measuring temperatures. Electronic weighing scales recorded changes in the sample weight every 60 seconds during reducing nickel from the oxide. The briquettes were soaked in the furnace until the loss of sample weight stopped. The resulting products were subjected to X-ray phase analysis.

A degree of nickel reduction at different temperatures after 15, 20 and 25 minutes of soaking was calculated by an equation:

$$\text{CB}(\%) = \frac{G \cdot \left[\frac{M_1}{M_1 + M_2} \right]}{M_3} \cdot 100 = \frac{G \cdot 16}{28} \cdot 100 = \frac{G \cdot 0.57}{M_3} \cdot 100,$$

Where G – loss of sample weight;

$M_1 = 16$ and $M_2 = 12$ – atomic weights of oxygen and carbon;

M_3 – weight of oxygen in the original sample

Treatment of steel in the ladle was studied under laboratory and workshop conditions. In the laboratory, steel was melted in a laboratory arc furnace, 10 tons capacity. A method of loading of nickel oxide into the arc furnace was experimentally determined and tested. Pallets 20–30 mm in diameter were made from the nickel concentrate, less than 0.5 mm fraction, obtained by beneficiation of polymetallic manganiferous ores and small coke.

The pallets were loaded into the furnace in two ways:

I – into the charge;

II – during the recovery period onto the heel of metal before building up slag.

The quantity of pallets was calculated to produce steel containing 1 % of nickel.

Experimental smeltings were carried out by conventional two-slag technology: the furnace was charged with a fusion mixture consisting of scrap metal, pellets, coke, and lime carbonate required to generate slag. When nickel concentrate pellets were used, a percentage of coke in the fusion mixture was increased providing for the amount of carbon necessary to reduce nickel from oxide state and for carbon loss. Pellets were placed closer to the slopes. The scrap metal used for smelting had the following composition: %: C – 0.275, Si – 0.267, Mn – 0.423, Cr – 0.175, Ni – 0.1, S – 0.027, P – 0.028, Fe – the rest.

The composition of the fusion mixture is shown in Table 2.

After the furnace was charged, the electrodes were dipped and the electric arc was lightened. The smelting time was 20 min.

By the end of the smelting period, slag was sintered in the furnace and some slag samples were taken for chemical analysis. Iron ore was loaded in batches to initiate a decarburation reaction. After five minutes of soaking, the slag was flushed out; metal and slag samples were collected for chemical analysis.

After removing oxidizing slag preliminary deoxidization with ferrosilicon was carried out in order to obtain a required percentage of silicon in the finished steel. After deoxidizers were added, lime carbonate and quartzite amounting 3 % of the metal weight were loaded into the furnace as slag-forming materials. After melting slag-forming materials and getting liquid slag the later was deoxidized by coke powder and ground ferrosilicon. Then slag and metal samples were collected for a chemical analysis.

The metal was tapped into the ladle. The ingot thus obtained was cut height wise into three equal parts. The resulting metal was analysed.

Table 2. Fusion materials for experimental smelting

Materials	Smeltings					
	1	2	3	4	5	6
Weight of briquettes	0.757	0.756	0.758	0.677	0.678	0.676
Composition of briquettes, % weight:						
Nickel concentrate	85	85	85	95	95	95
Coke	10	10	10	–	–	–
Bondings	5	5	5	5	5	5
Scrap metal weight, kg	9	9	9	9	9	9

For industrial tests of direct alloying of steel with nickel, steel was smelted in arc furnace DSP-40. Pellets for direct alloying were made of nickel concentrate and coke in stoichiometric proportion. The metal for test smelting had been certified according to the procedure adapted at “Stal NK” Ltd.

Results and Discussion

Thermodynamic calculations at different temperatures for Ni–O–*n*C system showed that the greatest reduction of nickel at the temperatures of 1073 K was obtained with 0.5 mole of carbon per 1 mole of NiO, and at the temperatures of 1573 and 1873 K the same result was achieved with 0.2 mole of carbon per 1mole of NiO. Complete reduction of nickel from its oxide in Ni–O–C–Fe system at the temperature of 1873 K takes 0.5 mole of carbon. If the amount of carbon in the system is increased over these values, iron begins to reduce from the oxide alongside with nickel (Figure 1).

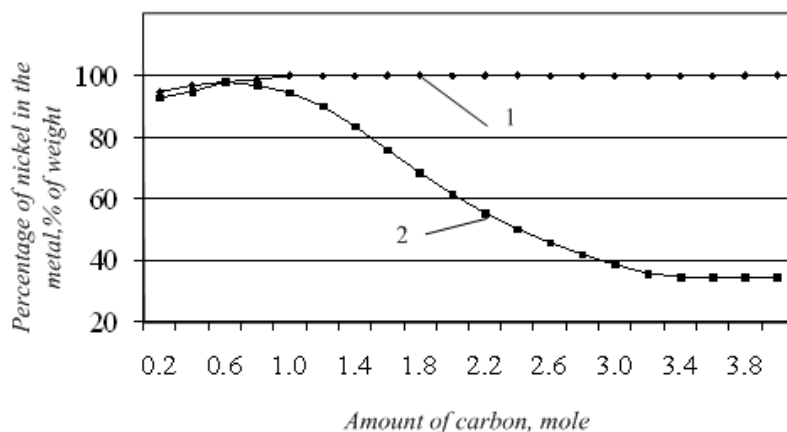


Figure 1. Dependence of nickel percentage in the metal on the amount of carbon in Ni–O–*n*C system at the temperature of 1073 K (1) and in Ni–O–*n*C–Fe system at the temperature of 1873 K (2)

Thermodynamic simulation showed that in Ni–O–*n*C system in Ni–O–*n*C system nickel can be completely reduced from the oxide at the temperature of 1073 K and in Ni–O–*n*C–Fe system it happens at the temperature of 1873 K.

A kinetic research and an X-ray phase analysis (Table 2) proved that at the temperatures of 1173 – 1473 K the complete reduction of nickel from its oxide takes 20–30 min, while at 1073 K the reduction process takes a longer time (70 min).

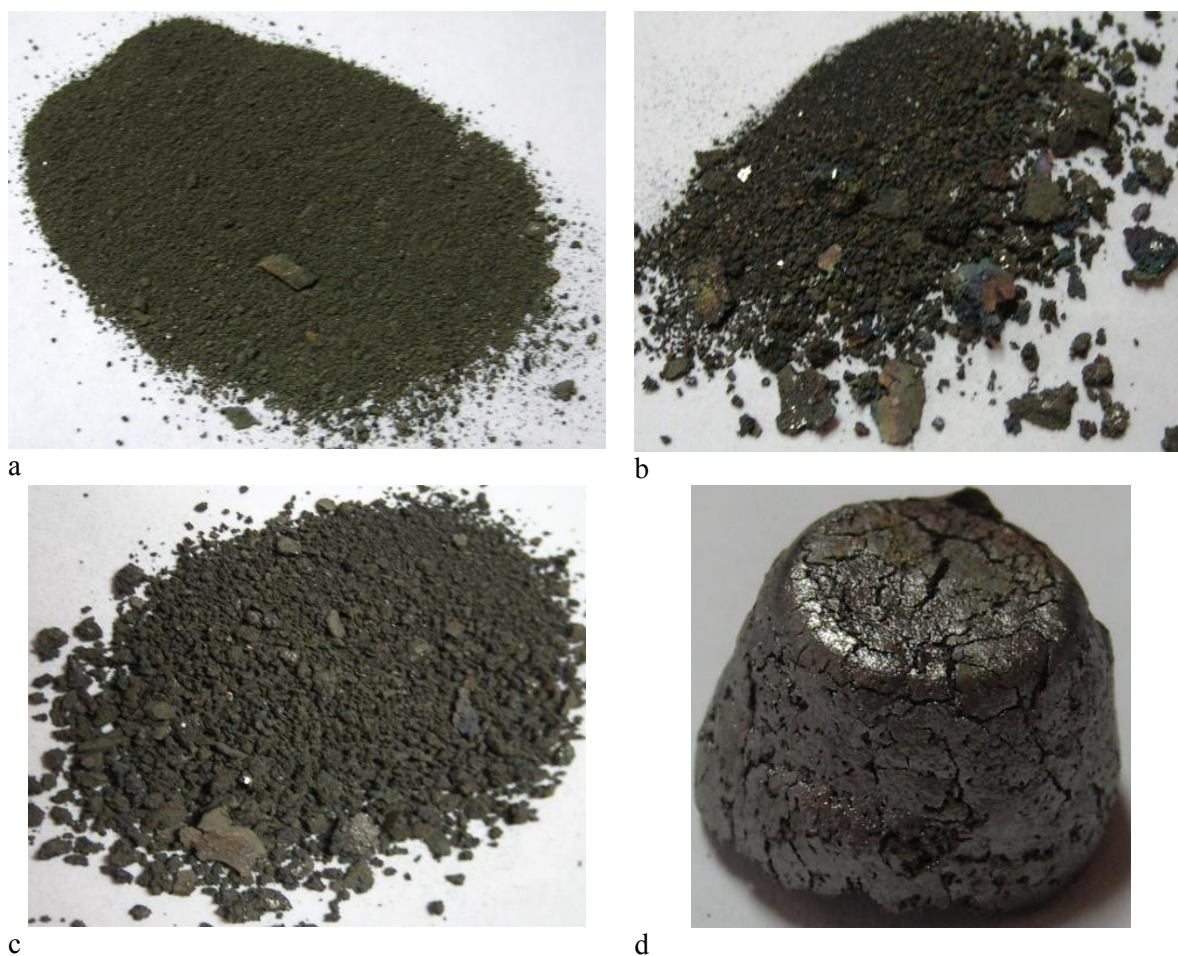
Samples which were soaked at the temperatures of 1173 – 1473 K are different in structure and color, and incorporate sintered bits with characteristic metallic luster. Dependences of nickel reduction rate on soaking time under such conditions demonstrate a more explicit increase which proves that the process becomes more active at a higher temperature (Figure 3). The X-ray phase analysis also proves this conclusion. The amount of the nickel oxide and the reducing agent decreases and the amount of nickel considerably increases.

Table 2. X-ray phase analysis

Soaking temperature, K	Phase composition	
	A lot	Some
1073	NiO, C	Ni*
1173	Ni	NiO, C
1273	Ni	NiO*, C*
1473	Ni	NiO*, C*

* – Found in a small quantity

Figure 2 shows samples after twenty minutes of soaking in the furnace at different temperatures.



a – 1073 K; b – 1173 K; c – 1273 K; d – 1473 K

Figure 2. Samples after 20 min soaking at different temperatures

According to the X-ray phase analysis at the temperature of 1473 K the percentage of nickel in the sample is greater and the amount of nickel oxide and carbon is lower than in the samples soaked at other temperatures.

Figure 4 shows the values of nickel reduction from its oxide. As we can see nickel reduction values greatly depend on the temperature of soaking nickel in the furnace.

The tests proved that the reduction of nickel from its oxide by solid carbon in the resistance furnace takes place at as low as 1073 K, but the process is slow. At 1173 K and above the reduction of nickel from its oxide is more intensive and takes less time.

Thus, when smelting steel in the electric arc furnace at the temperature range of 1173–1473 K, complete reduction of nickel from its oxide can take 20–30 min.

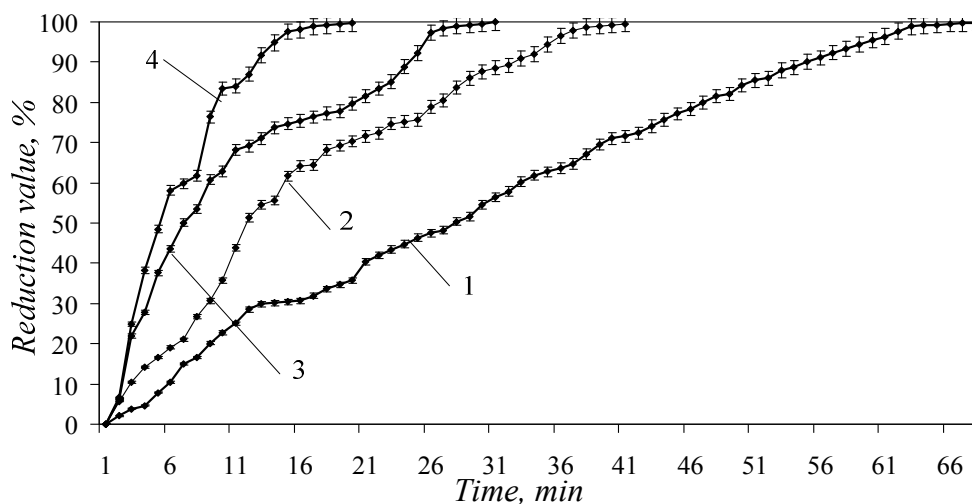


Figure 3. Dependence of nickel reduction values on isometric soaking time at the temperatures of 1073 K (1), 1173 K (2), 1273 K (3) and 1473 K (4)

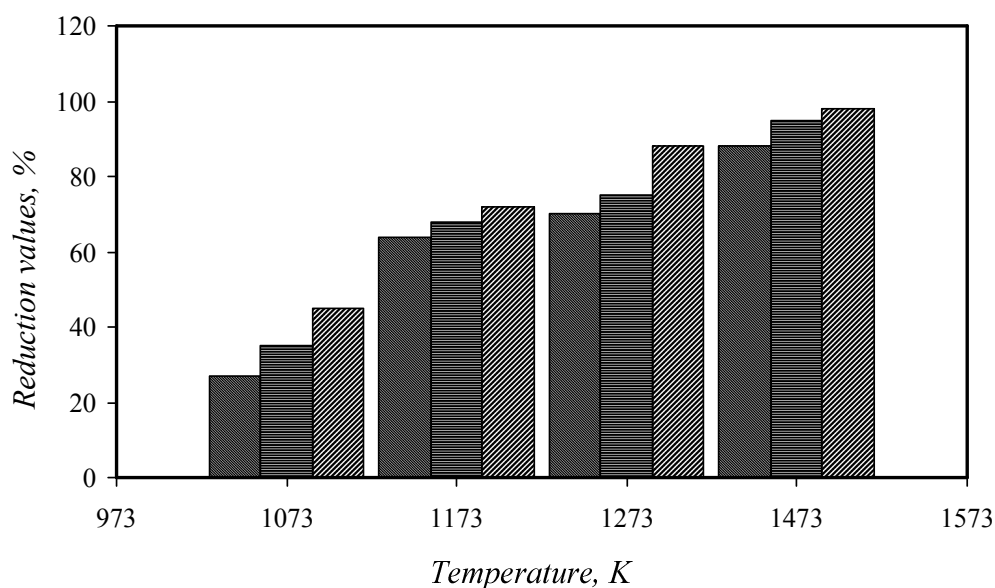





Figure 4. Dependence of nickel reduction values on temperature

(soaking time  – 15 min,  – 20 min,  – 25 min)

Laboratory tests resulted in finding the most effective method of loading the nickel oxide into the electric arc furnace. For smeltings 1 – 3, pellets made of nickel concentrate were used, for smeltings 4 – 6, pellets of nickel concentrate mixed with coke was applied. It was experimentally found out that the reduction of nickel is completed during smelting. Nickel output with pellets made of nickel concentrate and coke (smeltings 4, 5, 6) is as high as 97–98 %, while when pure nickel pellets are used (smeltings 1, 2, 3) it makes up 93–95 % (Table 3).

Table 3. Resulting data of alloying steel with nickel

Parameter	Values for smeltings					
	1	2	3	4	5	6
Ni percentage, %:						
– in scrap metal	0.1	0.1	0.1	0.1	0.1	0.1
– at the end of a smelting	2.85	2.79	2.83	2.91	2.94	2.93
– in the finished metal	2.85	2.79	2.83	2.91	2.94	2.93
– in the slag at the end of a smelting	0.144	0.207	0.165	0.084	0.057	0.063
Ingot weight, kg	9.96	9.97	9.95	9.98	9.97	9.95
Nickel reduction, % of weight	95.2	93.1	94.5	97.2	98.1	97.9

Nickel reduction produced by pellets with coke addition is higher and exceeds the values obtained with pellets of pure nickel concentrate by 3 – 5%.

When nickel is added at the beginning of the reduction process its reduction decreases. This is evidently caused by its partial evaporation in the arc zone as boiling temperature of nickel is relatively low.

Based on the experimental results obtained from thermodynamic stimulation of nickel reduction in the electric arc furnace we have developed a technology of direct alloying of chrome-nickel stainless steel 08(12)X18H10T. Smelting was performed by means of alloyed scrap remelting with complete oxidation. The furnace was charged with pellets made of nickel concentrate and coke. This technology has been tested in a steel smelting workshop of “Stal NK” Ltd. Industrial application of the developed technology of alloying steel with nickel using nickel concentrate showed that nickel reduction in the workshop conditions can reach 97 – 98 %.

The metal obtained in test smelting by the technology of direct alloying has been certified according to the procedure adopted at “Stal NK” Ltd, and it fully meets the requirements.

It is estimated that the use of nickel concentrate produced by hydrometallurgical beneficiation of polymetallic manganese ores and ferro-manganese nodules instead of pure nickel will reduce the cost of an alloying agent.

Conclusion

The theoretical and experimental research proved that nickel concentrate produced by beneficiation of polymetallic manganese ores is suitable for alloying steel with nickel in electric arc furnaces. The tests showed that direct alloying of steel is more effective when pellets consisting of nickel concentrate and small coke are fed into the charge, the optimal ratio of nickel oxide and reducing agent being 7:1. The resulting nickel reduction values obtained during the steel smelting is as high as 92–95 %.

References

- [1] Duan Yuping, Zhang Yahong, Wang Tongmin, Gu Shuchao, Li xin, Lv Xingjun 2014 *J. Materials Science and Engineering* **185** 86-93.
- [2] Santiago Sosa Haudet, Martín A. Rodriguez, Ricardo M. Carranza 2015 *J. Procedia Materials Science* **8** 21-28.
- [3] Nokhrina O I, Rozhikhina I D, Kichigina O Y, Goryushkina Y V, Rozevich A P 2012 *J. Steel in Translation* **42** 802-805.
- [4] Yan-li An, Hua-yun Du, Ying-hui Wei, Ning Wang, Li-feng Hou, Wan-ming Lin 2013 *J. Materials & Design* **46** 627-633.

- [5] Anand Kumar S, Ganesh Sundara Raman S, Sankara Narayanan T S N, Gnanamoorthy R 2012 *J. Surf. Coat. Technol* **206** 442.
- [6] Hu W, Yunxia W, Chenshuo M, Zhaolin Z 2014 *J. Applied Mechanics and Materials* **456** 406–410.
- [7] Babcsan N, Leitlmeier D, Degischer H.P, Banhart J 2004 *J. Advanced Engineering Materials* **6** 421–428.
- [8] Fedoseev S N, Mukhtar Z M 2015 *J. IOP Conference Series: Materials Science and Engineering* **91** 1–7
- [9] Mao D, Edwards J R, Harvey A 2006 *J. Chemical Engineering and Science* **61** 1836–1845.
- [10] Nokhrina O I, Rozhikhina I D, Proshunin I E, Khodosov I E 2015 *J. Steel in Translation*. **45** 295–300.
- [11] Rodzevich A P, Kuzmina L V, Gazenaur E G, Krashenin V I 2014 *J. AIP Conference Proceedings* **1623** 519-522.
- [12] Yang C C, Nakae H 2003 *J. Materials Processing Technology* **141** 202–206.
- [13] Ibragimov E A, Saprikin A A, Babakova E V 2014 *J. Advanced Materials Research* **1040** 764–767
- [14] Nokhrina O I, Rozhikhina I D, Hodosov I E 2015 *J. IOP Conference Series: Materials Science and Engineering* **91** 12-17.
- [15] Ferro P, Lazzarin P, Berto F 2012 *J. Materials Science and Engineering* **554** 122–128.
- [16] Fedoseev S N, Lychagin D V, Sharafutdinova A S 2014 *J. Advanced Materials Research*. **1040** 236-240.
- [17] Zhang W, Singh P, Muir D 2002 *J. Hydrometallurgy* **63** 127 – 135.